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P. 7

1,199,541

PATENT SPECIFICATION

DRAWINGS ATTACHED

1,199,541

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Index at acceptance:—C4 S(43Y, 70Y, 712, 714, 720, 725, 738, 756, 763, 78Y)

International Classification:—C 09 k 1/54

COMPLETE SPECIFICATION

Phosphor and Phosphor Coated Arc Discharge Device

We, SYLVANIA ELECTRIC PRODUCTS, INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 100, West 10th Street, Wilmington, Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phosphor-containing arc discharge lamps. It particularly relates to fluorescent lamps having a phosphor which can be energized by ultraviolet light to emit preferentially in the blue and red regions of the spectrum.

Phosphors that have been commonly used with arc discharge lamps include pyrophosphates, orthophosphates, halophosphates and tungstates. The light emitted from such phosphors is generally broad band, and thus can satisfactorily be employed in many blends when a particular emission is desired. However in some applications, it is desirable to use a lamp having a narrow band emission and maximum intensity at one or more particular wavelengths.

An example of such an application is a "Gro-Lux" lamp, used commercially for stimulating seed germination and increasing the rate of plant development and growth. The desired emission in such a lamp is that to which plant life is most responsive, namely, the blue and red spectrum bands. Plants utilize the energy in the blue band primarily for photosynthesis and chlorophyll synthesis, while the red band energy is necessary for vegetative growth.

In the prior art, this desired emission was obtained by blending two phosphors, one producing blue emission and the other red emission. Lead activated calcium magnesium tungstate is an example of a blue phosphor used, and tin activated strontium magnesium calcium orthophosphate an example of red. Since the two phosphors were blended into a single suspension prior to deposition on a lamp envelope, no unusual manufacturing problems were presented in their use. However the maintenance of the two phosphors was different, which resulted in a change in the ratio of blue to red energy emitted during the operating life of the lamp.

Maintenance refers to the output, or efficiency, of a phosphor after a certain period of operation, in comparison with its initial output. One of the causes of decrease in maintenance of a phosphor is the action of the mercury arc on the phosphor matrix. The arc radiation impinging on the phosphor particles lowers their efficiency with time. On different phosphor matrices, the rate of efficiency decreases varies, which results in the change of ratio mentioned above. Such a change is undesirable, since it results in inefficiency in the utilization of electrical energy and in its conversion to the spectral energy usable by the plants. Therefore it is preferred to maintain an optimum predetermined ratio of blue to red energy, as designed into the emission of the original lamps, throughout lamp life.

The single phase phosphor, hereinafter disclosed, emitting in both the blue and red bands, maintains a substantially constant ratio of blue to red energy throughout the useful life of the lamp.

In accordance with the invention, a phosphor suitable for use in such an arc discharge lamp comprises an alkaline earth metal magnesium silicate activated by divalent europium and divalent manganese. This phosphor emits preferentially in the blue and red regions of the spectrum. The phosphor matrix comprises either an orthosilicate or a pyrosilicate phase and its composition may vary within certain limits. When expressed as $xAO.yMgO.zSiO_2$, where A represents one or more of the alkaline earth elements calcium, strontium, and barium, the concentration of A atoms relative to Mg atoms preferably falls within the ratios of 3 : 1

[*Price 5s. 0d. (25p)*]

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to 1:2; the ratio of A+Mg atoms to Si atoms is preferably from 4:2 to 3:2. The atom fraction of Eu preferably varies from 0.0004 to 0.4, and the atom fraction of Mn from 0.0004 to 0.5. Compositions outside these preferred limits are generally too inefficient in the desired blue and/or red emission for the uses contemplated herein.

The preferred phosphor compositions of this invention have the general formula

$$A_a\ Mg_b\ Si_c\ O_d : \overset{+2}{Eu}_e,\ \overset{+2}{Mn}_f$$ where

a is between 0.5 and 3.0,
b is between 1.0 and 2.0,
c is between 1.0 and 2.0,
d is between 4.0 and 8.0,
e is between 0.0004 and 0.4,
f is between 0.0004 and 0.5.

The spectral energy distribution curves of phosphors prepared according to this invention exhibit two distinctly separate emission bands one in the blue region of the spectrum and one in the red when excited by ultraviolet radiation. Furthermore, in at least one of the fluorescent compositions disclosed herein the wavelengths within the blue and red bands at which maximum intensities occur can be varied by compositional variations of the large alkaline earth cations, that is, those of barium, strontium and calcium.

For example, in the orthosilicate phosphor of the type $A_3\ Mg\ Si_2O_8$, the maximum intensity or red band emission varies with the average ionic radius of the A atoms, that is, the large alkaline earth atoms of barium, strontium and calcium. As the average ionic radius is decreased, the wavelength at which maximum red emission occurs is shifted to longer wavelengths. The ionic radius of barium is larger than that of strontium which, in turn, is larger than that of calcium.

Table I, following, shows the wavelengths at which maximum emission occurs in the blue and red bands for several orthosilicate phosphors having a formula $A_{3-(e+f)}Mg\ Si_2O_8$ and illustrates the increase in the wavelength of maximum intensity of red energy as the average ionic radius of the large alkaline earth atoms, A, is varied.

TABLE I

	Phosphor	Ave. "A" Radius, Angstroms	Blue Band Peak, Nanometers	Red Band Peak, Nanometers
1.	$Ba_{2.86}MgSi_2O_8:Eu^{+2}_{0.04}, Mn^{+2}_{0.10}$	1.32	437	620
2.	$(Ba_{2.11}Sr_{0.75})MgSi_2O_8:Eu^{+2}_{0.04}, Mn^{+2}_{0.10}$	1.26	437	645
3.	$(Ba_{1.36}Sr_{0.75}Ca_{0.75})MgSi_2O_8:Eu^{+2}_{0.04}, Mn^{+2}_{0.10}$	1.18	443	670
4.	$Sr_{2.86}MgSi_2O_8:Eu^{+2}_{0.04}, Mn^{+2}_{0.10}$	1.11	458	685
5.	$Ca_{2.86}MgSi_2O_8:Eu^{+2}_{0.04}, Mn^{+2}_{0.10}$	0.99	475	700

In Table II the blue and red emission peaks and average ionic radius of the A atoms for another orthosilicate phosphor and for a pyrosilicate phosphor are shown.

TABLE II

	Phosphor	Average "A" Radius, Angstroms	Blue Band Peak, Nanometers	Red Band Peak, Nanometers
1.	$Ba_{0.76}Mg_2Si_2O_7:Eu^{+2}_{0.04}, Mn^{+2}_{0.20}$	1.22	400	690
2.	$(Ba_{0.38}Sr_{0.50})MgSiO_4:Eu^{+2}_{0.02}, Mn^{+2}_{0.10}$	1.17	437	660

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The measurements shown in Table I and II were all obtained at 2537 Angstrom excitation, which is commonly obtained from the arc of a fluorescent lamp. An enhanced luminescence is obtained under 3650 Angstrom excitation, such as is obtained from a high pressure mercury vapour lamp, in which the maximum intensities of emission still occur at about the same blue and red frequencies.

Manganese, alone, will not efficiently activate the $xAO.yMgO.zSiO_2$ compounds to fluorescence. However, when divalent manganese and divalent europium are used together as activators, useful emission is obtained in the blue and red bands. It is believed that an energy transfer occurs, from the europium to the manganese, to activate the manganese and yield the red emission band.

The phosphors herein disclosed may also be useful in phosphor blends where a high colour rendering index is desired, that is, to achieve a more balanced white light. An example of such a phosphor is

$$Ba_{0.66}Mg_2Si_2O_7 : \overset{+2}{Eu}_{0.01}, \overset{+2}{Mn}_{0.30}$$

which has a strong red emission peak at 690 nonometers and has a weak blue emission peak. This phosphor may be blended with conventional phosphors, which are usually deficient in red emission, to achieve a balanced white light.

Adjustment of the intensities of the blue and red peaks is obtained by compositional variation of the europium and manganese in the phosphors. In the previous example, the manganese concentration (after fraction) is 30.0% of the sum of A atoms plus activating atoms, which is 7½ times that of the europium concentration, with the result that the red peak is about 12 times higher than the blue peak. Consequently, a much higher percentage of the lamp's total emission is in the red band.

Above a manganese concentration of about 0.30 atom fraction, a diminution of the red emission occurs in this particular phosphor, and the total amount of red energy continues to decrease with increasing amounts of manganese. At about 0.005 or 0.01 atom fraction, the efficiency of red emission is generally too low to be useful. The minimum amount of manganese necessary to exhibit a red peak is about 0.0004 atom fraction.

An arc discharge device utilizing the phosphor of this invention can be a conventional fluorescent lamp, such as is shown in U.S. Patent No. 2,961,566 and in which ultraviolet radiation from an arc between two electrodes impinges on the phosphor disposed on the inner surface of the envelope.

In the accompanying drawings:

Figure 1 shows an arc discharge lamp, partly broken away, having a phosphor according to this invention disposed on the inner surface of the envelope.

Figure 2 is a spectral energy distribution curve of a barium magnesium orthosilicate phosphor, showing the blue and red emission peaks.

Figures 3 and 4 are similar curves for two different barium strontium magnesium orthosilicate phosphors.

Figure 5 is a spectral energy distribution curve of a barium magnesium pyrosilicate phosphor, showing the depressed height of the blue peak in relation to the red peak.

One embodiment of an arc discharge lamp in accordance with this invention, as shown in Figure 7, comprises a tubular glass envelope 1 and electrodes 2 at each end thereof. Within the envelope 1 is a fill including mercury. On the inner surface of the envelope 1, there is a coating 4 of an alkaline earth silicate phosphor, activated by divalent europium and divalent manganese. When an arc is struck between the electrodes 2, ultraviolet radiation therefrom impinges onto phosphor 4 and excites it to fluorescence. The resulting fluorescence can be predominantly blue and red, or predominantly red, depending on the phosphor composition.

In preparing the phosphors, the water content of the materials employed, for example manganese carbonate, silicic acid and basic magnesium carbonate, is first determined in order to compensate for sorbed water in formulating the blends.

Starting mixtures are prepared by dry blending the raw material and then firing the mixture, preferably in alumina trays, at about 600°C. to initiate the decomposition of the alkaline earth carbonates. The preferred mixtures are then fired at 1000 to 1300°C. for from 2 to 12 hours in a reducing atmosphere of 80% nitrogen and 20% hydrogen. After cooling in the reducing atmosphere, residual chloride is removed by a water wash. Ammonium chloride may be used as a flux to enhance the crystallinity of the fired product.

The following are offered as specific examples of the present invention:

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EXAMPLE I

$Ba_{2.83}MgSi_2O_8:Eu^{+2}_{0.02}, Mn^{+2}_{0.15}$

Material	Moles	Grams
$BaCo_3$	2.83	16.755
$3MgCo_3.Mg(OH)_2.3H_2O$	0.25	2.740
SiO_2	2.00	3.605
Eu_2O_3	0.01	0.106
$MnCo_3$	0.15	0.517
NH_4Cl	0.40	0.642

The weighed materials were intimately mixed by dry blending in a 100 ml. polystyrene mixing jar. Glass beads were added to aid in the blending. After mixing for 15 minutes the glass beads were removed and the mixture was placed in an alumina tray. The tray was fired at 600°C. for 30 minutes. The mixture was then placed in a silica tube, which was flushed with nitrogen for 5 minutes, and was then fired at 1200°C. for 4 hours in an atmosphere of 80% nitrogen and 20% hydrogen. After cooling to room temperature in the nitrogen-hydrogen atmosphere, the fired material was water-washed and dried. The resultant phosphor was pulverized, dispersed in a suitable liquid and coated on the inner surface of envelope 1 by processes commonly used in the industry.

Figure 2 shows the spectral energy distribution of this phosphor and particularly the strong blue and red emission. The blue emission peaks at 437 nanometers and has a relative energy of 48 units; the red emission peaks at 620 nanometers and has a relative energy of 41 units. In other regions of the spectrum, for example, the green region, the relative energy of emission is below 10 units.

In the following examples of other phosphor compositions in accordance with this invention, the same mixing and firing procedures were used as in example I.

EXAMPLE II

$(Ba_{2.08}Sr_{0.75})MgSi_2O_8:Eu^{+2}_{0.02}, Mn^{+2}_{0.15}$

$BaCo_3$	2.08	12.315
$SrCo_3$	0.75	3.322
$3MgCo_3.Mg(OH)_2.3H_2O$	0.25	2.740
SiO_2	2.00	3.605
Eu_2O_3	0.01	0.106
$MnCO_3$	0.15	0.517
NH_4Cl	0.40	0.642

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The spectral energy distribution curve of the barium strontium magnesium orthosilicate phosphor of Example II is shown in Figure 3. The blue and red peaks are at 437 and 645 nanometers and have relative energies of 29 and 46 units respectively. Special emission outside the blue and red bands is very low, less than about 5 units.

EXAMPLE III

$(Ba_{1.33}Sr_{0.75}Ca_{0.75})MgSi_2O_8:Eu^{+2}_{0.02}, Mn^{+2}_{0.15}$

$BaCO_3$	1.33	7.874
$SrCO_3$	0.75	3.322
$CaCO_3$	0.75	2.252
$3MgCO_3.Mg(OH)_2.3H_2O$	0.25	2.740
SiO_2	2.00	3.605
Eu_2O_3	0.01	0.106
$MnCO_3$	0.15	0.517
NH_4Cl	0.40	0.642

EXAMPLE IV

$(Ba_{0.38}Sr_{0.50})MgSiO_4:Eu^{+2}_{0.02}, Mn^{+2}_{0.10}$

$BaCO_3$	0.38	2.250
$SrCO_3$	0.50	2.214
$3MgCO_3.Mg(OH)_2.3H_2O$	0.25	2.740
SiO_2	1.00	1.802
Eu_2O_3	0.01	0.106
$MnCO_3$	0.10	0.345
NH_4Cl	0.40	0.642

The spectral energy distribution curve of the barium strontium magnesium orthosilicate phosphor of Example IV is shown in Figure 4. The blue and red emission peaks are at 437 and 660 nanometers and have relative energies of 25 and 22 units respectively.

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EXAMPLE V

$Ba_{0.76}Mg_2Si_2O_7:Eu^{+2}_{0.04}, Mn^{+2}_{0.20}$

$BaCO_3$	0.76	4.500
$3MgCO_3.Mg(OH)_2.3H_2O$	0.50	5.480
SiO_2	2.00	3.605
Eu_2O_3	0.02	0.211
$MnCO_3$	0.20	0.690
NH_4Cl	0.40	0.642

The spectral energy distribution curve of the barium magnesium pyrosilicate phosphor of Example V is shown in Figure 5, Emission in the blue region is greatly depressed and has a relative energy of only 3 units, in contrast to the red energy at 690 nanometers of 38 units.

WHAT WE CLAIM IS:—

1. A phosphor comprising an alkaline earth metal magnesium silicate activated by divalent europium and divalent manganese.

2. A phosphor according to Claim 1 wherein the host matrix has the general formula $xAO.yMgO.zSiO_2$, A representing an alkaline earth metal, and the ratio of A atoms to Mg atoms is between 3:1 and 1:2.

3. A phosphor according to Claim 2 wherein the ratio of A atoms plus Mg atoms to Si atoms is between 4:2 and 3:2.

4. A phosphor according to Claim 3 wherein the europium concentration is between 0.0004 and 0.4 atom fraction and the manganese concentration is between 0.0004 and 0.5 atom fraction.

5. A phosphor according to Claim 1 having the formula:

$A_aMg_bSi_cO_d:\overset{+2}{Eu}_e, \overset{+2}{Mn}_f$ where
A is calcium, strontium and/or barium,
a is between 0.5 and 3.0,
b is between 1.0 and 2.0,
c is between 1.0 and 2.0,
d is between 4.0 and 8.0,
e is between 0.0004 and 0.4 and
f is between 0.0004 and 0.5

6. A phosphor according to Claim 5 wherein the host matrix consists essentially of $A_{3-(e+f)}MgSi_2O_8$.

7. A phosphor according to Claim 5 wherein the host matrix consists essentially of $A_{1-(e+f)}Mg_2Si_2O_7$.

8. A phosphor according to Claim 5 wherein the host matrix consists essentially of $A_{1-(e+f)}MgSiO_4$.

9. A phosphor substantially as herebefore described with reference to Table I or II or any one of Examples I—V.

10. An arc discharge lamp having a light transmitting envelope and a phosphor according to any one of the preceding claims on the inner surface thereof.

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1199541 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

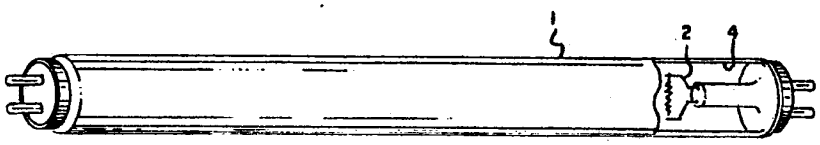


FIG.1

FIG.2

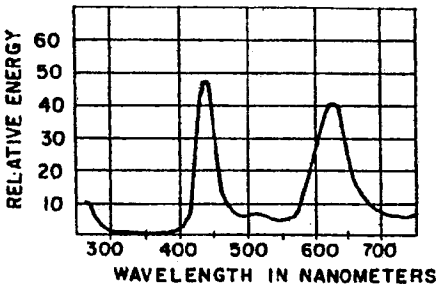


FIG.3

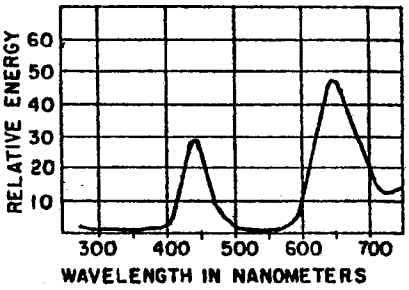


FIG.4

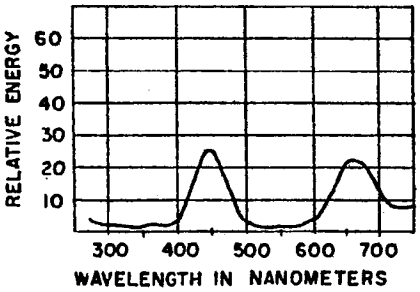
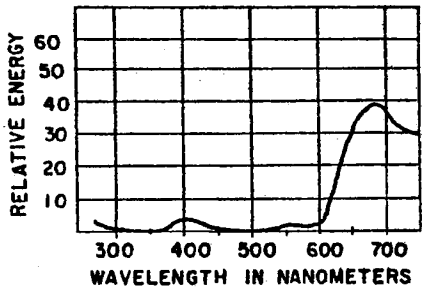


FIG.5



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